DEVELOPMENT OF GLASS COATING USING LIQUID EPOXIDISED NATURAL RUBBER

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ABSTRACT

The purpose of this study on glass coating using ENR is to study the development of glass coating. The ENRs are selected as their moderate cost, environmentally friendly, great adhesion properties, and easily produced thru a simple and quite rapid route using peroxy acid onto NR (Natural Rubber). The experiment including determine drying time of the LENR (Liquid Epoxidized Natural Rubber) coating at various ratio 1:15, 2:47, 2.5:50, 3:54, 4:60, 5:72 and compare drying at ambient temperature, at 40^0C and 50^0C and find out the physical properties of 25 mol% epoxidation LENR (Liquid Epoxidized Natural Rubber) coating viscosity, pH and density at various ratio. The adhesion test was also performed to determine how well LENR coating is bonded to the glass. In this research, the experiment was completed by determining the pH, viscosity and density of samples using Gas Pycnometer, pH meter and Viscometer. For the adhesion test a peel test method was conducted revealing the quality of coating. The experimental running proved that the most convenient sample coating compare from the entire composition ratio, sample E, ratio 4:60 is the coating with average viscosity 631cP and pH 8.55 which act as alkaline coating that possibly protect the glass and have less environment impact. The density of sample E coating is 0.895g/cm3. Furthermore, the cure time of the coating is 360s at 30^0C, 240s at 40^0C and 180s 50^0C that higher drying temperature result in short dry time. Also the hydrophobic property is an advantage for coating to protect glass. The result of this study is helpful to provide specific guidance in selection for developing high quality glass coating using LENR.

ABSTRAK

Tujuan kajian ini pada lapisan kaca menggunakan ENR adalah untuk mengkaji penambahbaikan lapisan kaca. Getah ENR telah dipilih kerana kos sederhana, mesra alam, sifat lekatan besar, dan mudah dihasilkan melalui kaedah yang mudah dengan menggunakan asid peroksi pada NR (Getah Asli). Eksperimen yang dilaksanakan termasuk menentukan masa pengeringan lapisan LENR (Cecair Epoxidized Getah Asli) pada pelbagai nisbah 1:15, 2:47, 2.5:50, 3:54, 4:60, 5:72 dan perbandingkan pengeringan pada suhu bilik, pada 40^0C dan 50^0C dan mengetahui sifat-sifat fizikal 25 mol peratus pengepoksidaan LENR (Cecair Epoxidized Getah Asli) kelikatan salutan, pH dan ketumpatan pada nisbah berbeza. Ujian rekatan telah juga dilakukan untuk menentukan kekuatan salutan LENR terikat pada kaca. Dalam kajian ini, eksperimen tersebut telah siap dengan menentukan pH, kelikatan dan ketumpatan sampel yang menggunakan alat Piknometer Gas, meter pH dan Meter Kelikatan. Untuk ujian rekatan kaedah mengupas telah dijalankan untuk mendedahkan kualiti salutan. Perjalanan eksperimen yang membuktikan bahawa sampel lapisan yang paling mudah bandingkan dari nisbah komposisi keseluruhan, sampel E, nisbah 4:60 lapisan dengan 631cP kelikatan purata dan pH 8,55 yang bertindak sebagai salutan alkali yang mungkin melindungi kaca dan mempunyai persekitaran kesan yang kurang. Yang ketumpatan salutan E sampel adalah 0.895g/cm3. Tambahan pula, masa pengeringan salutan 360-an pada 30 ^{0} C, 240s pada 40 ^{0} C dan 180s 50 ^{0} C yang lebih tinggi suhu pengeringan hasil dalam masa yang pendek. Sifat hidrofobik juga adalah satu kelebihan bagi salutan untuk melindungi kaca dari pembiakan bakteria dan lain-lain lagi. Hasil kajian ini adalah membantu untuk menyediakan panduan khas dalam pemilihan bagi salutan lapisan kaca yang berkualiti tinggi menggunakan LENR.

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LIST OF ABBREVIATIONS

ENR	Epoxidized Natural Rubber
LENR	Liquid Epoxidized Natural Rubber
NR	Natural Rubber
MRB	Malaysian Rubber Board
ABR	Acrylonitrile Butadiene Rubber
ASTM	American Society for Testing and Materials

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In glass industry, many challenges were faced due to producing a quality glass according to the customers preferance. According to the glass container industry, since the 1980s the glass container market has suffered a steady loss of market share to alternate plastic and can packaging. Imports of glass containers in 2001 total 27.9 million gross, compared with 30.6 million gross in 2000; and glass container exports total 11 million gross, compared with 8.8 million gross in 2000 (Highbeam Bussiness,2011). This prove that almost all kind of glass surface without coating actually experience breakage normally that is both a mess and a safety hazard. For instance, glass containers that bang into each other during filling, shipment, or in retail stores have lesser toughness without coatings. Low-maintenance glass coatings have been around for decades. Protective coatings have become more popular in the residential and commercial glass market during the last several years. The coatings are only now reaching the point of economic and technical growth.

1.1.2 Background of Epoxidized Natural Rubber

Currently Malaysian Rubber Board produces ENR which also called as Liquid Epoxidized Natural Rubber with the trade name Epoxyprene. There are two grades available, that is ENR-25 and ENR-50, with 25, and 50 mol % epoxidation, respectively. However the market and applications for ENR found to be limited. Thus efforts are being made to broaden the horizons of the usage and application of this rubber, especially in advanced engineering field. Coating with ENR is the easiest and the cheapest way to modify the strength of glass and all together reduces the material cost. Furthermore, the presence of oxirane group in ENR was found to be effective in causing specific interaction with a second polymer (Kallitsis and Kalfoglou, 1989).

The purpose of this study on glass coating using ENR is to study the development of glass in other words to improve the strength of glass. These ENRs are chosen as their moderate cost, environmentally friendly, great adhesion properties, and easily gained by means of the production line via a simple and quite rapid route using peroxy acid onto NR (Natural Rubber). A slightly changes in chemical structure in the presence of oxiranes making possible for ENR to possess other properties such as heat resistance, air permeability resistance, and stability due to chain re-arrangement.

1.2 PROBLEM STATEMENT

One of the marketing advantages the glass industry uses to sell its product is the perception by consumers that glass is a higher quality package than plastic. With glass's perceived quality and beauty, however, there is several characteristics that are viewed as negatives by bottlers, retailers, and the public especially the breakability of glass. Therefore to overcome the problems this research is conduct enhance the strength of glass. Besides glass experience breakage normally that is both a mess and a safety hazard. Thus handling the glass will reduce the unwanted accident to be occurred.

Recently, the Malaysian Rubber Board (MRB) officially annouced the price of the rubber rising, therefore the price of ENR also increasing. ENR is easy to be obtain yet it has disadvantage in its property toward the glass. It is not suitablenfor certain application since it is not transparent once ENR turn out to be thin film on glass. Hence,it is not suitable for optical glass, window glass and etc.

1.3 OBJECTIVES

The main objective of this research is to improve the glass coating using liquid epoxidized natural rubber.

1.4 SCOPE OF RESEARCH

In the current study, several significant parameters have been investigated. The detail of the scope is as below:

i. To investigate drying time of the LENR (Liquid Epoxidized Natural Rubber) coating at various ratio 1:15, 2:47, 2.5:50, 3:54, 4:60, 5:72 and compare drying at ambient temperature, at 40^{0}C and 50 ^{0}C.
ii. To find out physical properties of 25 mol% epoxidation LENR (Liquid Epoxidized Natural Rubber) coating viscosity, pH and density at various ratio.
iii. To determine the adhesion of a LENR coating on glass surface, a peel off test is performed.

1.5 RATIONALE & SIGNIFICANCE

The rationale of this research project is to provide empirical evidence to find out the finest quality LENR coating material on glass surface at various ratios 1:15, 2:47, 2.5:50, 3:54, 4:60, 5:72 at levels of 25 mol% epoxidation. The results of this research would signify the identification of an alternative coating between the various ratios to perform a safe and protective layer on the glass.

One of the important products of chemical modification of natural rubber is the epoxidized natural rubber, ENR. Through chemical modification, natural rubber properties would be enhanced. Hence, ENR has the potential to be further exploited for its usage as advanced materials in glass industry.

1.6 THESIS OUTLINE

The outline of this thesis is presented as a schematic form as displayed in Figure 1.1, and the brief description of each individual chapters is showed at the remainder of this chapter.

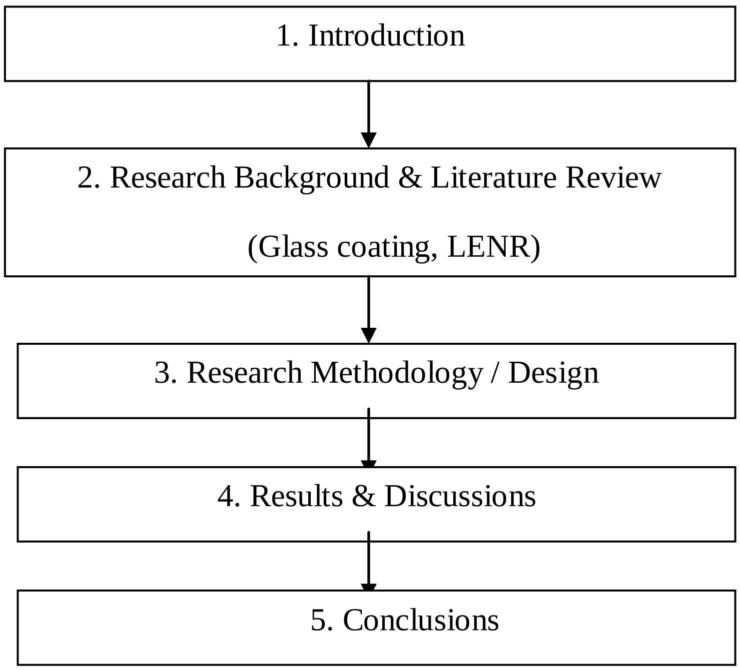

Figure 1-1: Road map for the thesis

Chapter 2 describes literature review and research background of ENR including the related fields of glass coating. It also involves LENR's properties along with technological challenges involved in the glass coating industry.

Chapter 3 is a detailed description of research methodology or design for this research that revealing about the various materials used and the methods of characterizing the samples and standards. Furthermore, it includes LENR quality analysis techniques which are the pH, viscosity and density including the drying time and adhesion property of several ratios at 25 mol% epoxidation.

Chapter 4 is about the results and discussions of this research. The detail reports on experimental result along with the discussion of the quality coating material liquid epoxidized natural rubber on the glass surface.

Chapter 5 delivers the conclusion of this research where the contribution of main findings and also the recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 EPOXIDATION OF NATURAL RUBBER

Epoxidised natural rubber (ENR) is a derivative of natural rubber produced by chemical modification. It was not until the mid 1980s that pure samples of ENRs were prepared and their properties fully recorded (Gelling, 1999).For the most general natural rubber originated from the plant Hevea brasillensis. The main natural rubber producers in the world are Malaysia, Thailand and Indonesia. The major uses of a natural rubber are for production of tires, molded goods and mechanical parts while the lesser uses are the chemical derivatives of rubber. Enhanced properties of natural rubber for certain applications can be made via chemical modifications. This is possible because of the existence of double bonds (C=C) in the natural rubber polymer chain that perform as simple olefin. One of the important products of chemical modification of natural rubber is the epoxidized natural rubber, ENR. Reacting natural rubber with peroxy formic acid can produce ENR 46 (Figure 2.1). It was stated that 1-90% epoxidation of the natural rubber is possible, however only 3 types of ENR were considered as commercial standard. These are ENR-10, ENR-25 and ENR-50 where the integers designate 10, 25 and 50-mole % of epoxide included into the natural rubber chain respectively (C.H. Teoh, 2006). Through chemical alteration, natural rubber properties would be improved. Therefore ENR also display properties that are the same as a specialty elastomer such as decrease in air permeability, that is similar to a butyl rubber and increment in oil resistance, which is comparable to Acrylonitrile Butadiene Rubber (ABR) (C.H. Teoh, 2006) including Figure 2.2 shows the structure of Epoxidised Natural Rubber (ENR).

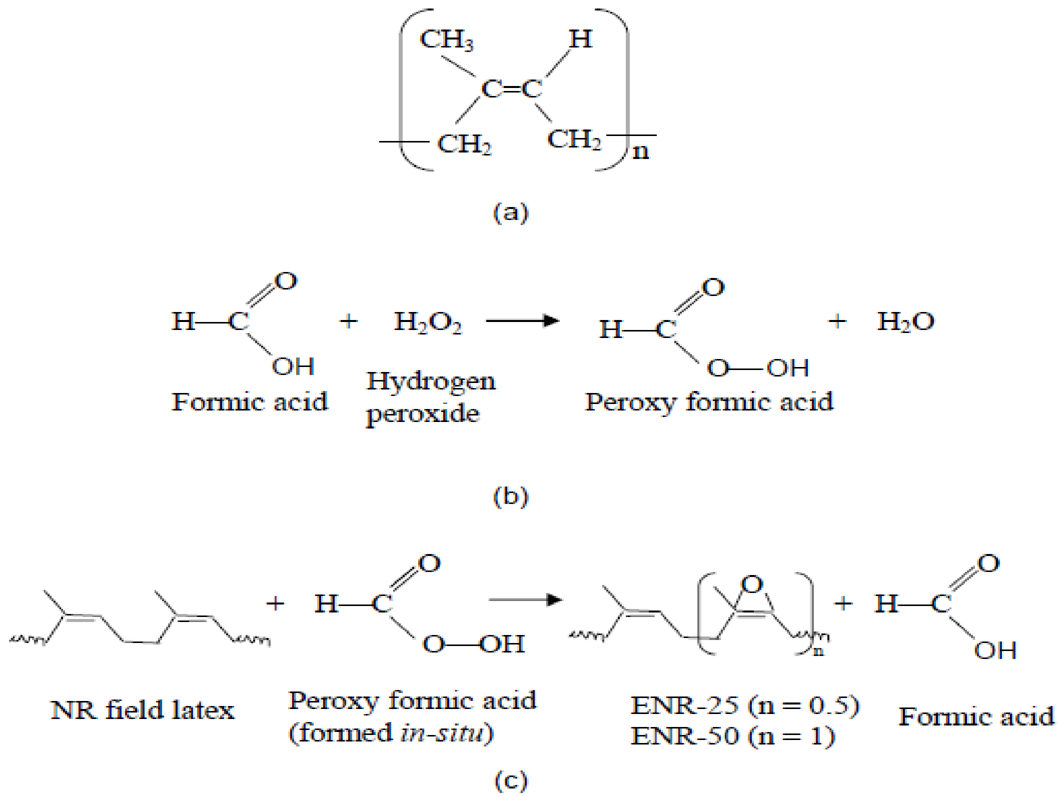

Figure 2.1: (a) Structure of natural rubber, cis-1, 4-polyisoprene, (b) formation of peroxy formic acid and (c) the production of ENR

Source: C.H. Teoh (2006)

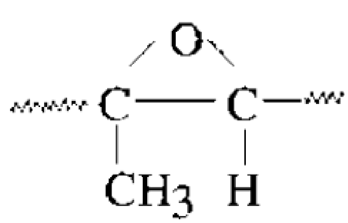

Figure 2.2: Structure of Epoxidised Natural Rubber (ENR)

Source: Ratnam et al.,(2001)

The mechanical properties of natural rubber (NR) are generally superior to those of synthetic rubbers. Moreover, NR cannot compete with the specialty synthetic elastomers with regards to such properties as gas permeability and oil resistance like mention above. The epoxidation reactions recognized for the chemical modification of NR, that guide to the development of epoxidised natural rubber (ENR) .These modified polymer have enhanced oil resistance and decrease gas permeability, at the same time as maintaining most of the properties of NR (M.Zurina,2007)

Table 2.1: Typical Properties of ENR (Ismail, 2004).

Properties	ENR 10	ENR 25	ENR 50
Glass transition temperature, T_g (ºC)	-60	-45	-25
Specific gravity	0.94	0.97	1.03
Mooney viscosity,$M_{L,1+4}$ (100ºC)	90	110	140

2.2 APPLICATION OF EPOXIDIZED NATURAL RUBBER

Epoxidized Natural Rubber, ENR shows both rubber and special elastomer characteristics that can be modified for various usages. Some of the potential commercial uses of ENR with respect to its special characteristics are use for Tires, non-slip flooring, sports shoe soles, Hoses, seals, blow-out preventors, milking inflation, connector and tubing, as for silica and pigments reinforcements characteristic is used in cosmetics, color coding, adhesives, cover for PVC conveyor belt and finally as for the characteristic of gas permeability the bladders, inner tubes, and tire liners is used (C.H. Teoh, 2006). Besides the proposed commercial uses shown, ENR has the potential to be further exploited for its usage as advanced materials such as in blends, additives and fuel cells applications.

2.3 GLASS COATING

According to Oxford dictionary the definition of glass coating is a layer or film spread or paint over a surface for protection or decoration purpose. Coatings applied to glass surfaces are an essential part of manufacturing in all segments of the glass industry. Without coatings, not only would many glass products not have the properties that make them so widely used, they would be impossible to make.(Mark D. Allendorf,2001).

Coating is an essential method to enhance the property of the material especially in glass. The important role for coatings in strength is to improve mechanical barrier in term of modulus and abrasion resistance and water barrier compressive residual stress, flaw healing especially in cut edges. Glass is an essentially a strong material. Nevertheless, due to the presence of defects, practical strength of glass articles is significantly lower than the theoretic strength.

An effective method of strengthening glass is highly desirable for making stronger, safer, lighter, or cheaper glass products. Strengthening of glass is traditionally achieved using techniques like thermal tempering and ion exchange. Yet, both approaches create compressive stress on the glass surface for strengthening.(Mei Wen and S.W. Carson,2008, “A Study on the Strengthening Glass by Polymeric Coatings”)

2.3.1 Significant of Glass Coating

This report also points to the significance of coatings in the glass industry. Without coatings, countless glass products would not have the properties that which no longer valuable, useful and many would also be impossible to make. Examples can be found throughout the industry. For instance, Because of its abrasiveness, glass fiber could not be formed into products such as fiberglass insulation and composites for automobiles without protective and lubricating coatings.

The studied increases in energy efficiency achieved by low-E and solar-control glass (a nearly twofold increase in the R value of a dual-pane window over uncoated glass) are due entirely too sophisticated application of multiple coatings. The high throughputs of today's container lines would not be possible without lubricious coatings; coatings also increase the burst strength of glass containers threefold. New glass products at the forefront of the industry, such as "smart windows" and flat-panel displays, depend on coatings to accomplish their functionality. The glass industry aspiration document, Glass: A Clear Vision for a Bright Future (Jan. 1996), identifies that the "development of innovative uses of glass is a target of the industry's future." This report also points to the importance of coatings in the glass industry, Examples of some of the many innovative glass products that use coatings are given in Table 2-3. The Glass Technology Roadmap (Sept. 1997), includes a partial list of industry-wide product categories essential to broadening the market for glass products. (Coatings on Glass Technology Roadmap Workshop,2000)

Table 2.2: Current products apply coatings and functions of the product. (Source: R. Gordon, Harvard University)

Current Products	**Function**
Low-E window glass	Energy-conserving windows
Solar control + low-E glass	Windows in large buildings, hot climates
Photovoltaics	Solar electricity
Flat-panel displays	TV, computers
Electrochromic mirrors	Automatic rear-view mirrors in cars
Touch-panel controls	Appliances
Anti-reflection TV	picture framing
Anti-static	Copiers
Defogging Supermarket freezers	windows in vehicles
Anti-abrasion	Bar-code readers
UV protection	Reduced fading of fabrics and art work

2.4 EFFECT OF COATING

There are `many factors lead to the production of perfect coating material such as the pH, thickness, temperature, viscosity of coating, and organic coating formulation itself and moisture of the coating. These effects are crucial in many industries concern on these qualities and durable of coating with the requirement of customer.

2.4.1 Formulation of Organic Coating

The preparation of the organic coating has effect upon on the chemistry of polymer chain formation and molecular weight. The crucial form of the polymer chain, its length, shape, and configuration determines the properties and physical characteristics of the coating, such as durability, hardness, and adhesion.

2.4.2 Coating Viscosity

Apart from that, the viscosity of the coating affects the coating especially during the transition from the wet to the cured state (dried) is particularly important. As the coating cures, its viscosity fluctuates and increases, and its mobility or flow decreases. If the epoxy is not properly formulated, flow of the coating into the substrate microstructure may be hampered, adversely affecting adhesion and producing a number of voids and holidays in the film. The low viscosity coating flows better is easier to roll or brush, saturates surface of glass quickly, and penetrates more evenly in fact drying period taken is short compare to more viscous coating. There are two methods of temporarily thinning epoxy. One is to heat the mixture and the other is to add solvent to the mix. The aim of both methods is to reduce the coating viscosity. (Gaynes and Norman, 1977)

2.4.3 Temperature Coating

Usually glass is exposed to ambient temperature. Thus, the capability of heat resistance of glass coating is crucial to protect the glass especially country that have weather changes need coating that resistance at neither extremely high nor low temperature; the coating will become soft and fluid or become harden and tear into piece, and even will be susceptible to deterioration. Therefore, coating material should be able to withstand the maximum temperature of glass, steel or plastic otherwise the coating will be failed.

2.4.4 Moisture of coating

Moisture is directly significant as the temperature of coating. Unless moisture is present, there is possible chance to have permanent loss of adhesion. The existence of high temperature only causes temporary loss of adhesion, but immediately after the organic coating cools, adhesion can be regained. Therefore, high temperatures will generally produce loss of adhesion when moisture is present. Equally, moisture alone produces loss of adhesion over time, but high temperatures help to accelerate the disbondment process (Enrique Vaca-Cortés., Miguel A. Lorenzo., et al., 1998).

2.5 ADHESION

According to online oxford dictionary adhesion means the action or process of adhering to a surface or an object like the adhesion of the epoxy or other organic coating to the steel to avoid corrosion of steel. Adhesion strength between the coating and the substrate is a crucial factor in successful attaching and long-lasting stability of any coated implant. A varies range of methods is used to evaluate to adhesion of the coating (K.L. Mittal, 1976).

2.5.1 Tape Test

The most usually applied methods employed to assess adhesion strength of coating on substrate include tensile test (pull-out test) (D.M. Liu, Q. Yang and T. Troczynski, 2002) and scratch test (M.F. Hshieh, L.H. Pwerng and T.S. Chin, 2002), scratch test and tape test. A variation of peel adhesion test was carried out by McDonald et al. Known that the porous microstructure and the high surface roughness of these coatings peel test deems a better method the reason is the strongly influences such as glue infiltration which are expected in peel off test (P.A. Steinman, Y. Tardy and H.E. Hintermann, 1987).

These methods include the peel-off method by using adhesive tape for instance 3M Scotch brand tape, pressure sensitive tape and etc. are performed based on ASTM standard-American Society for Testing and Materials. This standard test method set up a procedure for determining whether the adhesion of a polymer coating to a glass, steel and plastic material is an adequate level.

In this study the tape used was 3M emulsion water based acrylic adhesive tape, the direct pull-off method have to do with ASTM D 3359 Standard Test Methods for Measuring Adhesion by Tape Test. Even though the lack of a fully satisfactory analytical model of its mechanics (J. Williams, 1996), the tape test is normally used to quantitatively assess the quality of adhesion of coatings to substrates.

2.6 DRYING TEST

The drying process of coatings and paints plays a vital role in substrate or in other word the coating material is crucial in protection of object (for instance; steel, plastic or glass) since many cases the object to protect is immobilized. The understanding of the drying processes provides the development of suitable drying systems process for each different application.

Based on the researchers named J.I. Amalvy, and C.A. Lasquibar a previous work has been reported on the application of drying period of coating in industry identified to be mixed with the petrol or any interferometry to the drying of paints with relatively long drying times. (P.A. Facciaa, O.R. Pardinia, J.I. Amalvya,b, N. Capc, E.E. Grumelc, R. Arizagac, M. Trivic,2009).

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

In this particular chapter, a detail of experiment framework will be presented, also included materials to be used, description of experimental adhesion test, drying test, density test, pH and viscosity analysis and also sequence of experimental procedures. The main purpose of this study is to determine the adhesion and physical properties of the LENR as a glass coating material on the glass surface. As well, the part of studies is also to identify the drying time of LENR at various ratio. Adhesion test is performed by conducting the tape test.to determines how well a coating is bonded to the glass. Commonly used measuring techniques are performed with tape test adhesion tester.

3.2 MATERIALS AND EQUIPMENT

The following chemicals will be engaged for the preparation of coater (LENR) and painting process;

i) Epoxidized Natural Rubber (ENR-25,25mol% epoxidation)
ii) Toluene (C_7H_8)
iii) Isopropyl alcohol, IPA (C_3H_8O)

Below table is the function of each component in the experiment setup